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Fiber Wetting and Coatings for Composite Fabrication

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Graphite fibers resist wetting when immersed in most molten metals. They must be coated with a material that can be wet and that also protects the fibers against chemical degradation during processing. A model of the graphite fiber surface is proposed, and a brief history of coatings that have been investigated for wetting is presented. The titanium-boron chemical vapor deposition process is discussed as well as the graphite-metal interface that results from that process. Finally, Aerospace-developed air-stable coatings and their processing are described. The technique used by

DD FORM 1473

19. KEY WORDS *(Continued)*

20. ABSTRACT *(Continued)*

Aerospace is a solution-coating process. The fibers are passed through appropriate organometallic solutions followed by either hydrolysis or pyrolysis of the organometallic compounds to form the desired coating on the fiber surfaces. Fibers have been coated with selected oxides, nitrides, and carbides, using this technique. Also, a modification of this technique can be used to coat fibers with amorphous carbon. These coatings can be applied to other fibers as well as graphite, and some are easily wet by metals. In addition, the coatings are expected to be useful for controlling the fiber matrix bond strength in ceramic matrix composites.

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I. INTRODUCTION

Graphite fiber-reinforced metals are emerging as a valuable new class of structural materials. Graphite-magnesium and graphite-aluminum are uniquely suited to solve many of the material problems associated with spacecraft. They combine high specific strength and stiffness with near-zero coefficients of thermal expansion, high electrical and thermal conductivity, and no outgassing or contamination. Graphite-copper has been identified as an excellent candidate material for structural applications at temperatures in the 500-800°C range.

The basic difficulty with the fabrication of these materials is that the graphite fibers resist wetting when immersed in most molten metals. The fibers must be coated with a material that facilitates wetting and protects the fibers against chemical degradation during processing and use. The coatings that will be discussed in this report were specifically developed for graphite fibers but have also been applied to FP alumina and Nicalon silicon-carbide fibers. These coatings not only facilitate wetting and protect the fibers in metal matrices but are also expected to be useful for controlling the fiber-matrix bond strength in ceramic matrix composites.

II.   THEORY AND EXPERIMENTAL RESULTS

Figure 1 is a schematic representation of the graphite fiber surface proposed by S. Chwastiak. Most of the graphite planes are aligned in the fiber direction. However, some plane edges are exposed at the fiber surface. The surfaces of high modulus fibers such as P100 are smooth and have most graphite planes aligned parallel to the surface with few edges exposed. Lower modulus fibers such as T300 are rougher and have more edges exposed at the fiber surfaces (Fig. 2). Because the edges of the graphite plane are chemically much more reactive than the plane faces, the lower modulus fibers are more reactive than the higher modulus fibers. The increased reactivity of lower modulus fibers makes them easier to wet. However, chemical reactions can occur at the active sites, resulting in brittle carbides that act as stress-risers and seriously degrade the strength of the fibers.

Table 1 presents a partial list of coatings that were investigated in the late 1960s and early 1970s to facilitate the infiltration of liquid aluminum into graphite fiber bundles.[1] The degree of success varied, but even the more successful methods were not pursued because of various experimental problems. The fabrication process that was selected for further development relies on the coating of the fibers with both titanium and boron by chemical vapor deposition (CVD)[1] (Fig. 3). Most graphite fiber-reinforced metals now being produced in the United States are made by this technique. It is applicable to most metal matrices of interest including magnesium, aluminum, and copper.

There are some basic problems associated with the CVD technique. The process is inherently expensive because only a small amount of the starting material reacts to coat the fibers. The furnace walls are also coated, and most of the starting material, which is highly corrosive, does not react at all and must be scrubbed for disposal along with the corrosive reaction by-products. However, the most serious problem is that the titanium-boron coating is not air stable and therefore cannot be exposed to air before immersion in the molten metal. This severely limits the shape of material

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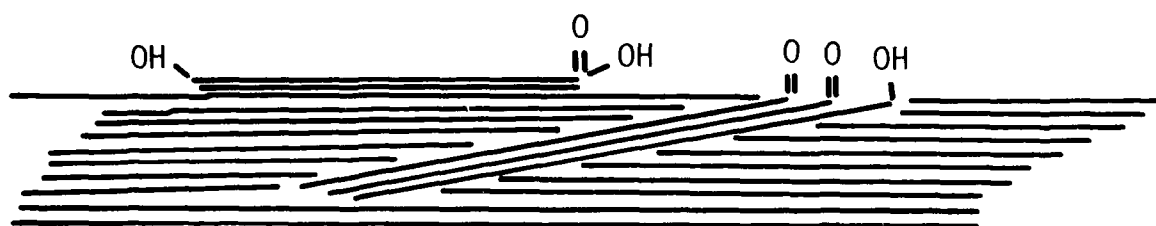Fig. 1. Graphite Fiber Surface Schematic

T300   P100

Fig. 2.   SEM Photomicrographs of T300 and P100 Graphite Fibers

Table 1. Graphite Fiber Coatings for Liquid Aluminum
         Infiltration

COATING	METHOD OF APPLICATION	RESULTS
NICKEL	ELECTROPLATING	PRESSURE INFILTRATION AT 700°C RESULTED IN ALUMINIDE FORMATION AND LOW STRENGTH IN COMPOSITE
NICKEL	ELECTROLESS DEPOSITION	CONTINUOUS CAST (draw through) WIRE RESULTED IN 60% ROM STRENGTH
SILVER	ELECTROPLATING	INCOMPLETE FIBER COATING
COPPER	ELECTROPLATING	PRESSURE INFILTRATION AT 700°C RESULTED IN LOW STRENGTH COMPOSITE
COPPER	ELECTROPLATING	LIQUID INFILTRATION AT 700°C FOR SHORT CONTACT TIMES RESULTED IN 75% ROM STRENGTH
TANTALUM	CHEMICAL VAPOR DEPOSITION	LIQUID INFILTRATION AT 1100°C BY DRAW THROUGH RESULTED IN 90% ROM

Table 1. Graphite Fiber Coatings for Liquid Aluminum
Infiltration (Continued)

| COATINGS	METHOD OF APPLICATION	RESULTS
BOROCARBON	THERMAL DECOMPOSITION OF $B(C_2H_5)_3$ AT 700°C	VACUUM CASTING PRODUCED POOR WETTING AND LOW STRENGTH
BORON	THERMAL DECOMPOSITION OF DIBORANE AT 700-750°C	VACUUM CASTING PRODUCED POOR WETTING AND LOW STRENGTH
SILICON	THERMAL DECOMPOSITION OF SILANE AT 800°C	WETTING ACHIEVED ON POLYCARBON CORP. C1000 AND HERCULES HT FIBERS
TITANIUM CARBIDE	REDUCTION OF $TiCl_4$ WITH METHANE AT 750-1700° C	MEASURED THICKNESSES FROM 0.06 TO 1.3 μm, BUT ONLY LIMITED INFILTRATION AT 50 psi
ZIRCONIUM CARBIDE	CHEMICAL VAPOR DEPOSITION	NO INFILTRATION BY MOLTEN Al 6061 AT 1 atm
SODIUM TIN MAGNESIUM	SEQUENTIAL LIQUID METAL BATH TREATMENT	COMPLETE INFILTRATION AND 95-100% ROM STRENGTH
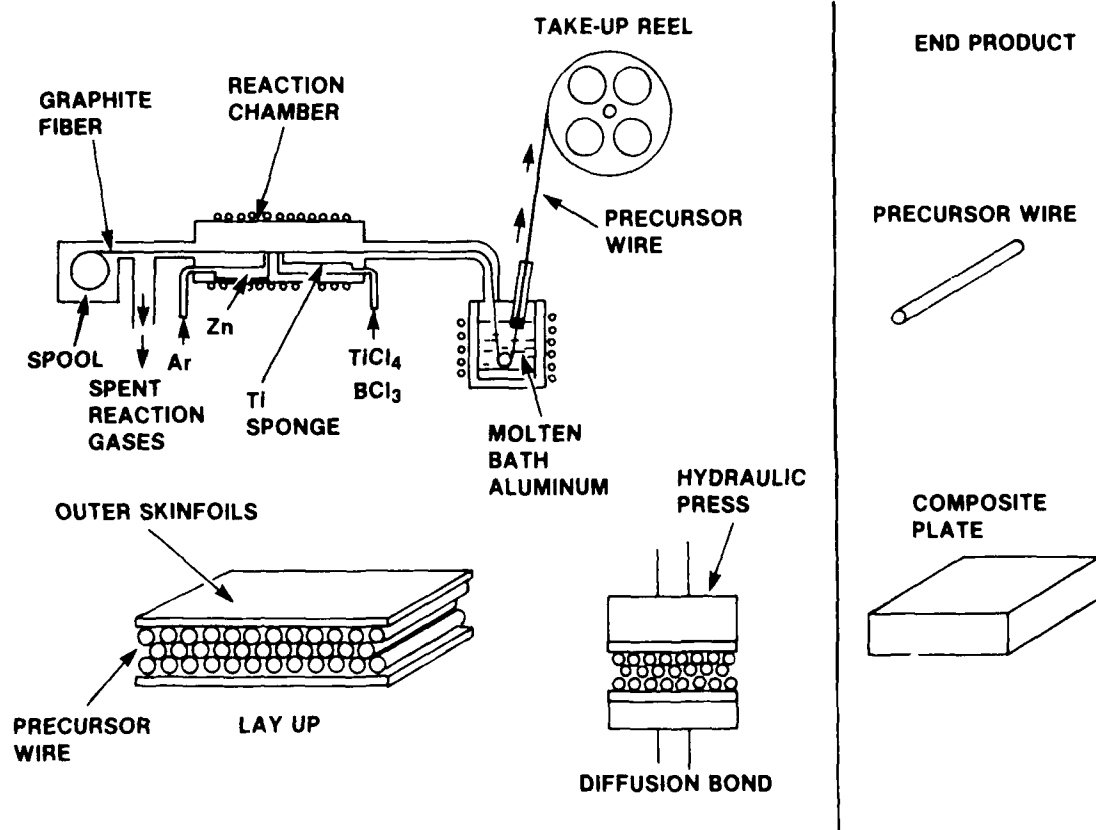
Fig. 3. Schematic of Composite Fabrication

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that can be fabricated. Only continuous fiber-reinforced metal wire has been successfully made by this process to date. This wire must then undergo costly secondary fabrication to produce useful structural shapes such as plates or tubes. Also, the number of final shapes is limited because the wires are not very flexible.

In order to avoid these problems, we have developed air-stable coatings that permit the metal-matrix fabricators to take advantage of all of the technology developed for graphite-epoxy. In our approach, coatings are deposited on the fiber surfaces from a solution containing various organometallic compounds. The fibers are simply passed through these solutions followed by either hydrolysis or pyrolysis of the organometallic compounds to form the desired coating. The coated fibers can be treated as prepreg material and can be filament wound or used with a fugitive binder for selective reinforcement. The coated fibers are then incorporated into the metal by casting near-net shapes.[2] An additional advantage is that the fiber volume fraction can be controlled to a much greater degree than is now possible.

Our air-stable coatings were developed based on an understanding of the nature of the interface in graphite-aluminum made by the titanium-boron CVD process. Scanning Auger microprobe (SAM) analysis (Fig. 4) revealed that there was a thin oxide layer between the fiber and matrix[3] (Fig. 5). A pure aluminum matrix results in Al_2O_3. When magnesium is present in the alloy (e.g., Al 6061), a mixed magnesium-aluminum oxide is formed. The oxygen apparently comes from the sizing that is applied to the fibers by the manufacturer for ease of handling. This oxygen-containing sizing is not completely removed before processing. Indeed, a sizing that contains oxygen has been found to be necessary in order for wetting to occur. When the sizing is completely removed before processing, metal infiltration into the fiber bundle is very poor. Moreover, the oxide phase provides bonding between the fiber and matrix. These observations resulted in the hypothesis that a suitable oxide layer on the fiber surfaces would promote wetting. We found that a thin layer of silicon dioxide does indeed facilitate wetting of the fibers by molten magnesium.

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Fig. 4. SEM of Composite Indicating Locations
for SAM Analysis on Fiber and on Matrix
Above and Behind Fiber

FIBER

MAGNESIUM AND
ALUMINUM OXIDE

TYPICAL
FRACTURE
PATH

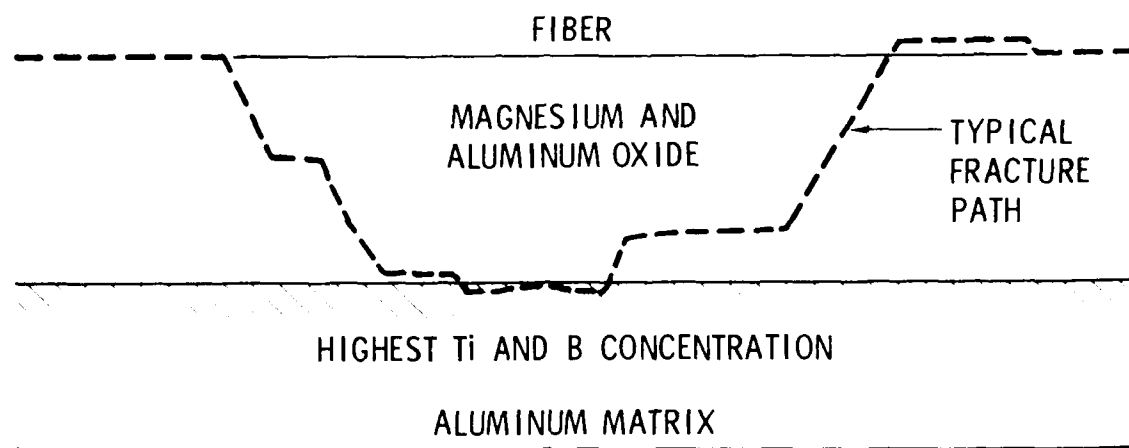HIGHEST Ti AND B CONCENTRATION

ALUMINUM MATRIX

Fig. 5.   Interface in Graphite-Aluminum Made by TiB Process

We developed a continuous process for coating graphite fibers with various oxides with the use of organometallic solutions (Fig. 6). In this solution-coating process, the fibers are passed sequentially through a furnace to vaporize and remove the sizing and then through an ultrasonic bath containing an organometallic solution. The coated fibers next go through a chamber containing flowing steam in which the organometallic compound on the fiber surface is hydrolyzed to oxide. They then pass through an argon-atmosphere drying furnace in which any excess solvent or water is vaporized and any unhydrolyzed organometallic compounds are pyrolyzed.

The process makes use of a class of organometallic compounds known as alkoxides,[4] in which metal atoms are bound to hydrocarbon groups by oxygen atoms. The general formula is $M(OR)_x$, where R is any hydrocarbon group (e.g., methyl, ethyl, propyl), and x is the oxidation state of the metal atom M. These alkoxides hydrolyze when exposed to water vapor in accordance with the general equation:

$$M(OR)_x + \frac{x}{2} H_2O \rightarrow MO_{x/2} + xROH$$
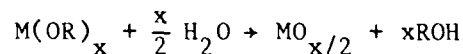
As an example, the alkoxide tetraethoxy silane (also called tetraethyl-orthosilicate) is hydrolyzed by water as follows:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$
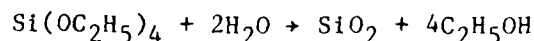
Alkoxides can also be pyrolyzed to yield oxides. Tetraethoxy silane pyrolyzes as follows:

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2C_2H_5OH + 2C_2H_4$$
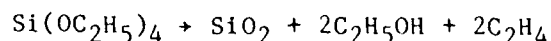
Some of the elements for which alkoxides are commercially available are Si, Al, Ti, Li, Na, K, Zr, and B. Most alkoxides can be dissolved in toluene, and solutions that produce various mixed oxides can be made easily. By controlling the solution concentration and the time and temperature of immersion, it is possible to control the uniformity and thickness of the resultant oxide coatings.

SIZING BURN-OFF
FURNACE

HYDROLYSIS
CHAMBER

DRYING
FURNACE

TAKE-UP
REEL

FIBER
TOW AS
RECEIVED

ORGANOMETALLIC
SOLUTION IN
ULTRASONIC TANK

STEAM

Ar

COATED
FIBERS

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH\uparrow$$

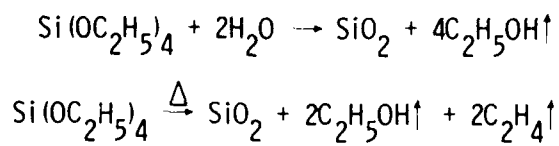$$Si(OC_2H_5)_4 \xrightarrow{\Delta} SiO_2 + 2C_2H_5OH\uparrow + 2C_2H_4\uparrow$$
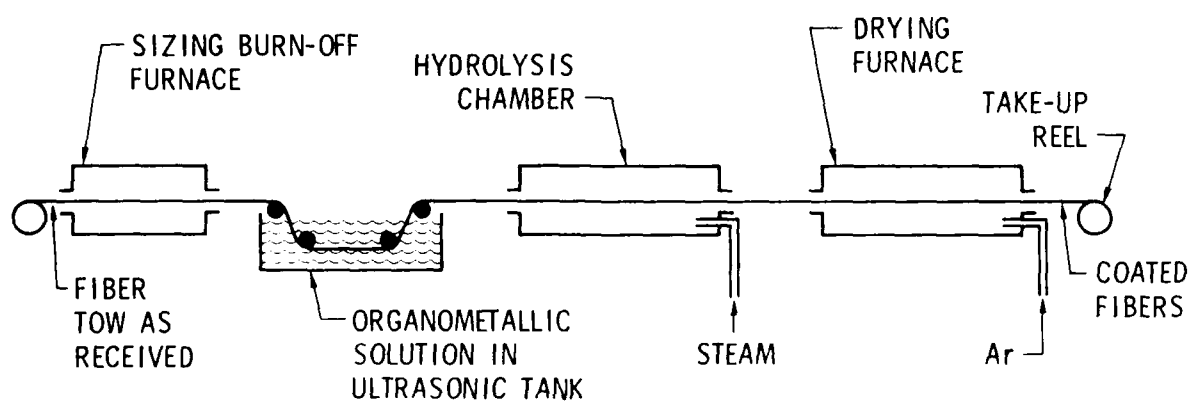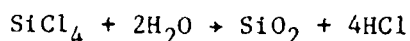
Fig. 6. Solution Coating Process

The chlorides of Si, Ti, and B are less stable than their oxides and are easily hydrolyzed by water or water vapor. For example,

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

These chlorides are generally more reactive than alkoxides and are also soluble in toluene. Therefore, a mixture of chlorides and alkoxides can be used to control the reactivity of the toluene solution.
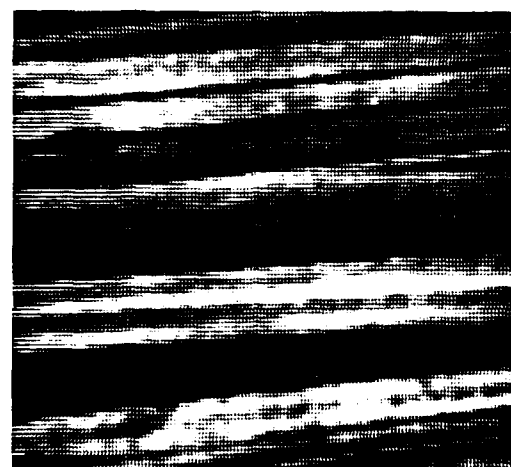
Examination of the coated fibers with SAM reveals a uniform oxide coating on all of the filaments (Fig. 7). SAM depth profiles indicate that the thickness of the oxide coatings on the fibers varies from 700 to 1500 Å with an average value of approximately 1000 Å (Fig. 8). These thickness values are verified by transmission electron microscopy (TEM) (Fig. 9). Both electron and x-ray diffraction indicate that the oxide coatings are amorphous. As can be seen from the SAM depth profile, the oxide coatings contain some carbon. This carbon originates in the carbon fiber, not in the organometallic compound or solvent, because similarly applied coatings on FP alumina fibers contain no carbon.

When silicon dioxide-coated T300 graphite fibers are immersed in liquid magnesium, the metal wets the fiber coating and infiltrates into the fiber bundles.[5] Wetting is the result of a reaction between the molten magnesium and the silicon dioxide coating (Table 2). SAM analysis indicates that silicon is present at the fiber-matrix interface and that the interfacial layer consists of magnesium silicate and magnesium oxide (Fig. 10). This has been confirmed by secondary ion mass spectroscopy.

T300 fibers have very high strength but only moderately high stiffness (35 msi). Composites reinforced with much higher modulus fibers are required for some applications. Graphite fibers (P100) manufactured from mesophase pitch have a modulus of 100 msi and can be coated with oxides by our solution-coating process. SAM analysis indicates similar coating thickness and uniformity as for T300 fiber coatings. However, when the oxide-coated P100 fibers are immersed in molten magnesium, very little magnesium adheres to the

SEM OF COATED FIBERS   SILICON MAP

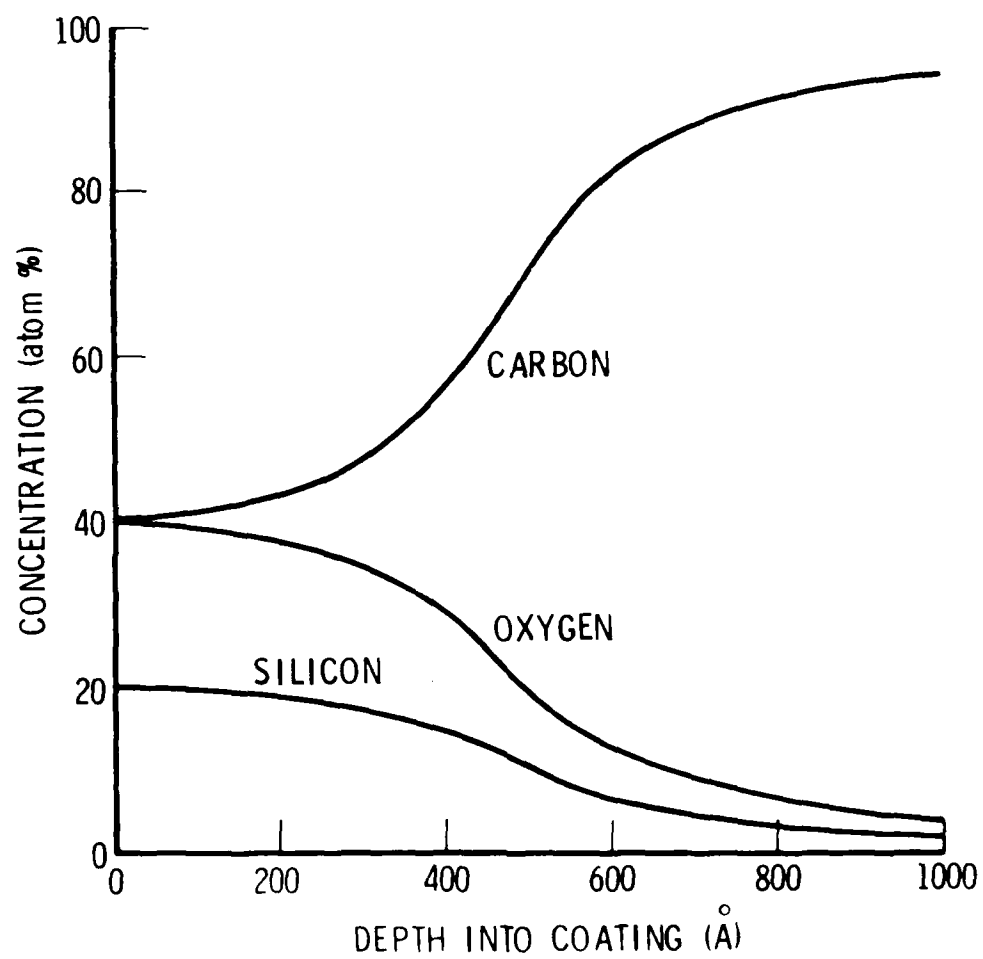Fig. 7.   SAM Mapping of SiO_2 Coated Thornel 300 Graphite Fibers

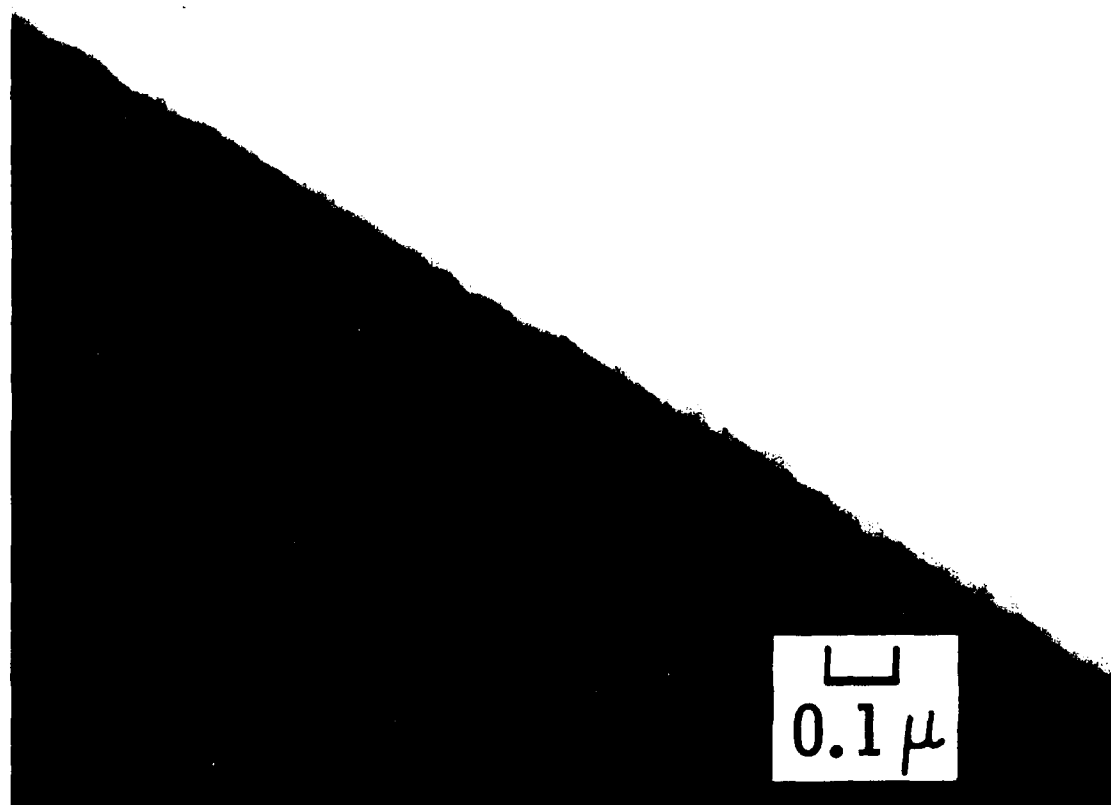Fig. 8. Concentration Profiles of SiO_2 Coatings on Graphite Fibers

Fig. 9. TEM Photomicrographs of a T300 Graphite Fiber Coated with
Silicon Dioxide

Table 2.   Reactions of Mg with SiO_2

$$2Mg + SiO_2 \rightarrow 2MgO + Si \qquad \Delta G°_{670°C} = -76 \text{ kcal}$$

$$MgO + SiO_2 \rightarrow MgSiO_3 \qquad \Delta G°_{670°C} = -23 \text{ kcal}$$

$$2Mg + 3SiO_2 \rightarrow 2MgSiO_3 + Si \qquad \Delta G°_{670°C} = -122 \text{ kcal}$$

$$2MgO + SiO_2 \rightarrow Mg_2SiO_4 \qquad \Delta G°_{670°C} = -28 \text{ kcal}$$

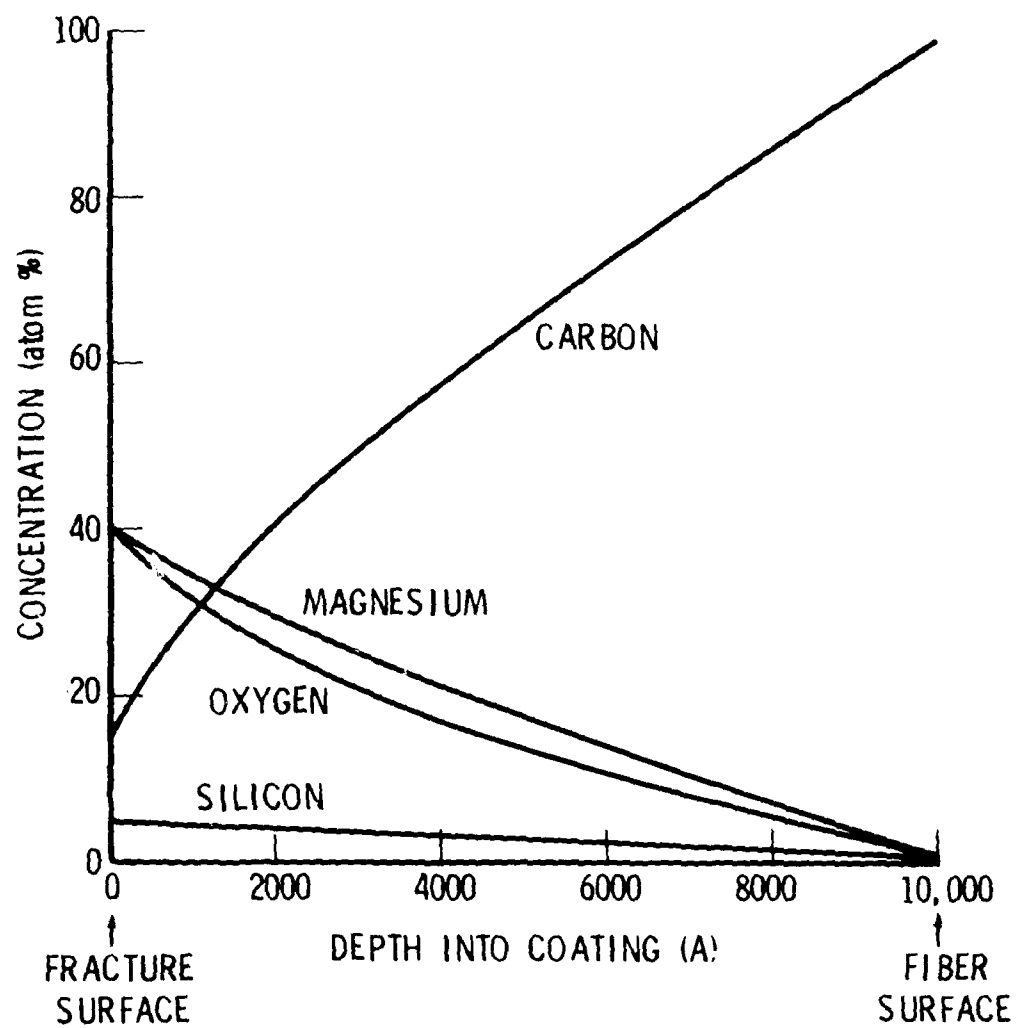$$2Mg + 2SiO_2 \rightarrow Mg_2SiO_4 + Si \qquad \Delta G°_{670°C} = -104 \text{ kcal}$$

Fig. 10. Concentration Profiles of Coating Adhering to Fibers
After Fracture

fibers. SAM analysis reveals that when the fibers are immersed in liquid magnesium, the oxide coating separates from them, indicating that the oxide coating does not adhere to the P100 fibers as well as to the T300 fibers.

As previously discussed, the difference in adhesion is the result of differences in both the surface morphology and chemical reactivity of the two fibers. However, we succeeded in improving the adhesion between the P100 fibers and the oxide coatings, which permitted the production of magnesium reinforced with P100 fibers. In our approach, a thin amorphous carbon coating is first deposited on the P100 fibers.[6] After they are coated, the P100 fiber surfaces resemble those of the T300 fibers, to which the oxide coating adheres very well. The carbon coating is applied to the P100 fibers by passing the fiber bundles through a toluene solution of petroleum pitch. This is followed by evaporation of the solvent and pyrolysis of the pitch to yield the amorphous carbon coating (Fig. 11). The P100 fibers are then coated with silicon dioxide by our solution-coating process. When the fibers are then immersed in molten magnesium, the result is good wetting and infiltration.

We have deposited other coatings besides oxides and amorphous carbon on the fiber surfaces. When alkoxides are pyrolyzed in ammonia (Fig. 12), nitrides rather than oxides are formed. Even though the free energies of the reactions shown in Fig. 12 are positive, they are much less positive than when the starting material is an oxide. Also, by using flowing ammonia, there is always a large excess of ammonia that drives the reactions to proceed in the direction shown. SAM analysis has indicated that the nitride coatings do contain a small amount of oxygen. These nitride coatings do not promote wetting by metals but are expected to find use in modifying the bond strength in ceramic matrix composites. Experiments in this area of study are currently under way in our laboratory.

Silicon-carbide coatings can also be applied to fibers with the use of organometallic polymer precursor compounds. These compounds are currently being investigated as precursors to make silicon-carbide fibers.[7] However, the same compounds can be used for coatings (Fig. 13). As an example, we have used polycarbosilane (a precursor for Nicalon fibers) dissolved in toluene to
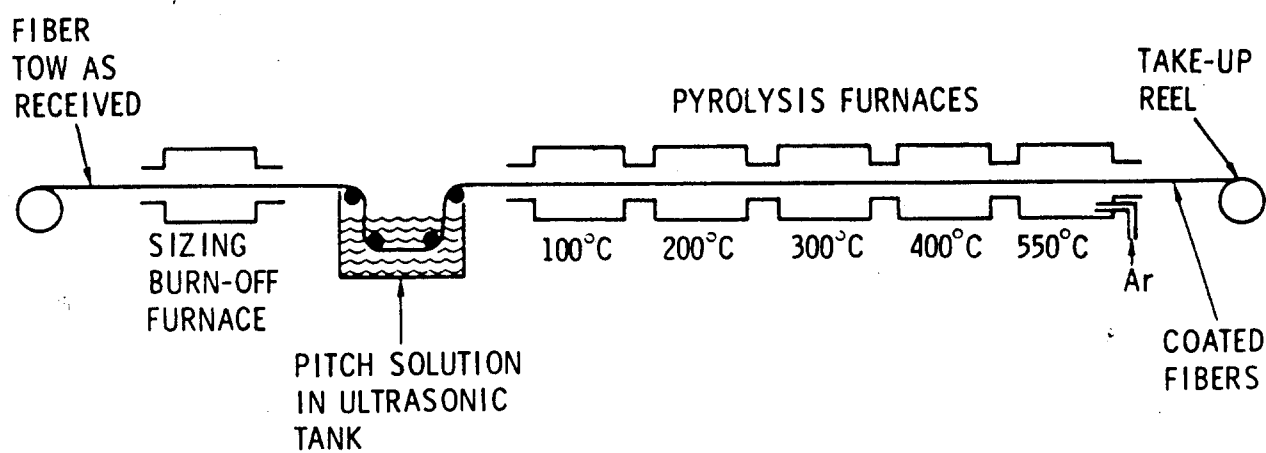
FIBER
TOW AS
RECEIVED

PYROLYSIS FURNACES

TAKE-UP
REEL

SIZING
BURN-OFF
FURNACE

100°C   200°C   300°C   400°C   550°C

Ar

PITCH SOLUTION
IN ULTRASONIC
TANK

COATED
FIBERS

Fig. 11.   Process for Coating Fibers with Amorphous Carbon

PYROLYSIS
FURNACE (1000°C)

SIZING BURN-OFF
FURNACE

TAKE-UP
REEL

GRAPHITE
FIBER
TOW

COATED
FIBERS

Ar
OR
AIR

ORGANOMETALLIC
SOLUTION
IN ULTRASONIC
TANK

NH_3

$$3Si(OC_2H_5)_4 + 4NH_3 \xrightarrow{1000°C} Si_3N_4 + 12C_2H_5OH$$

$$Ti(OC_4H_9)_4 + NH_3 + 1/2H_2 \xrightarrow{1000°C} TiN + 4C_4H_9OH$$
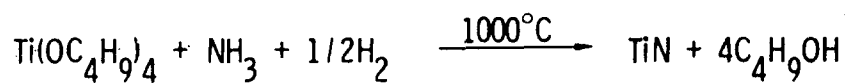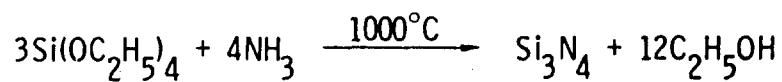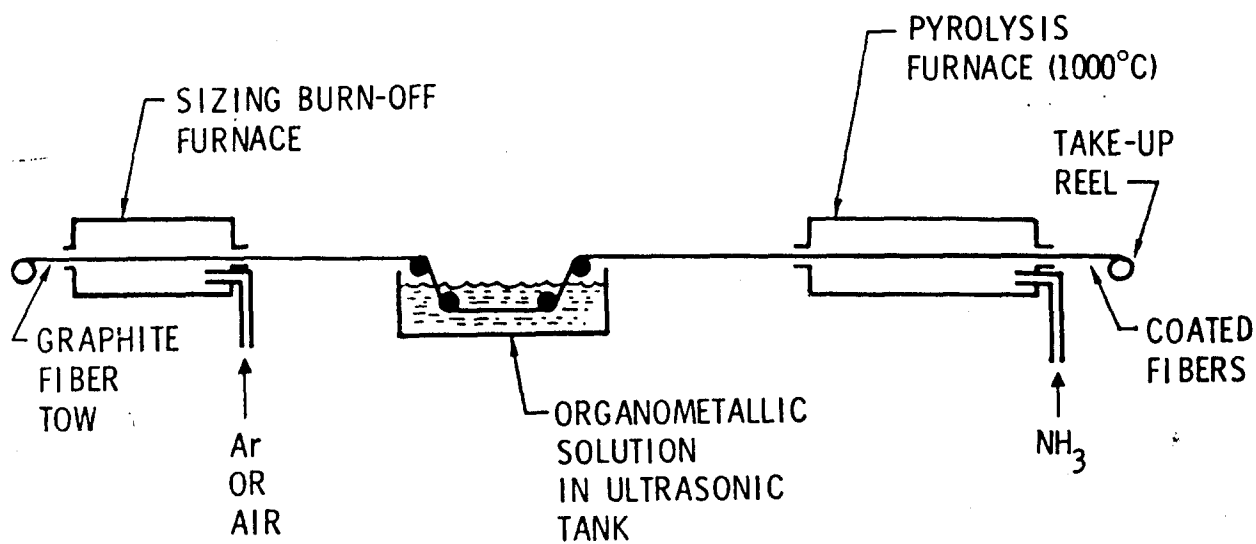
Fig. 12. Process for Coating Fibers with Nitrides

30

FIBER
TOW AS
RECEIVED

PYROLYSIS FURNACES

TAKE-UP
REEL

SIZING
BURN-OFF
FURNACE

100°C   200°C   300°C   500°C   1000°-
                                     1200°C   Ar

ORGANOMETALLIC
PRECURSOR
SOLUTION

COATED
FIBERS

$$\begin{bmatrix} \begin{array}{cc} CH_3 & H \\ | & | \\ Si & - C - \\ | & | \\ H & H \end{array} \end{bmatrix}_n \xrightarrow{1200°C} nSiC + nCH_4 + nH_2$$
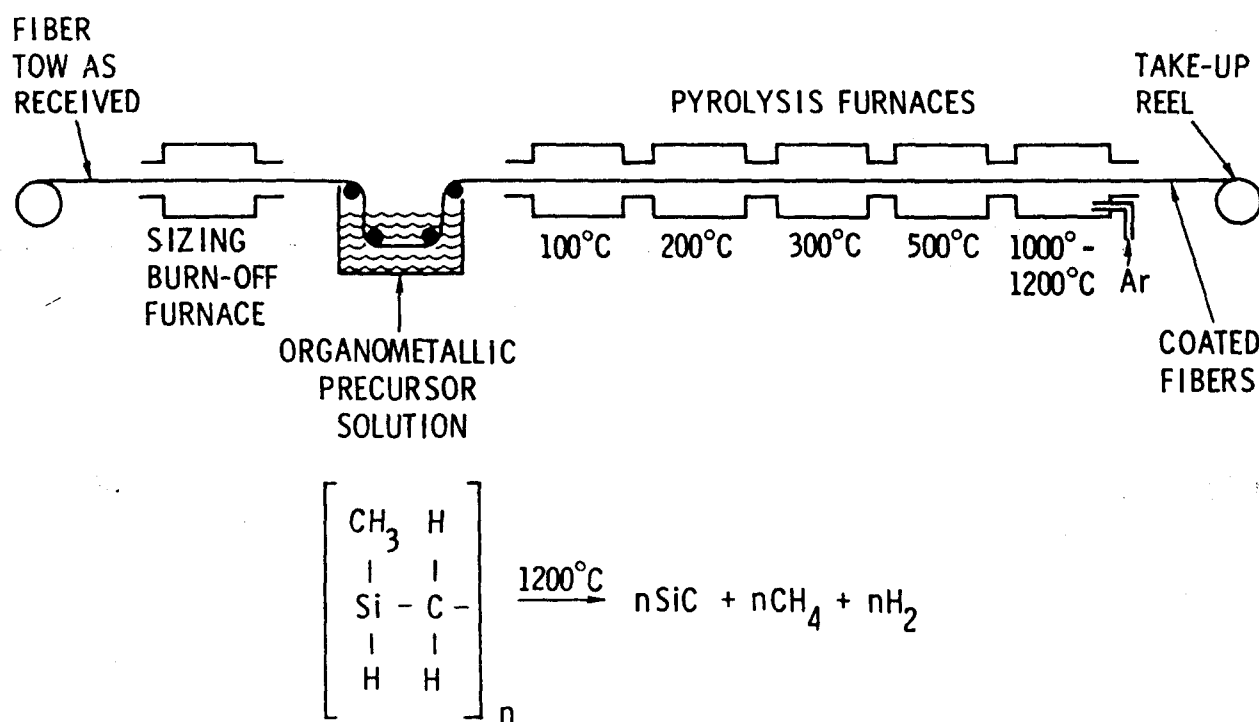
Fig. 13.   Process for Coating Fibers with Silicon Carbide

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coat graphite fibers. The polycarbosilane is then pyrolyzed to silicon carbide on the fiber surfaces. Electron diffraction confirms the presence of silicon carbide. However, SAM analysis reveals that some oxygen is also present in the coatings as well as silicon and carbon.

These silicon-carbide coatings are wet by molten copper containing a small amount of titanium. Titanium carbide has been identified at the interface by TEM analysis. It appears that the wetting is the result of a reaction between the silicon carbide and the titanium in the alloy to form titanium carbide. We are currently investigating the use of other alloy additions to copper as well as other organometallic precursors to SiC.

We have also extensively investigated air-stable coatings for graphite-aluminum. A mixed boron-silicon oxide is the most effective coating applied from organometallic solutions to date. However, even though the outer surface of the fiber bundles are well wet with either aluminum 6061 or aluminum-10% magnesium alloy utilizing this coating, infiltration of the alloy into the fiber bundle is very poor. We have recently found that ultrasonic vibration of the aluminum alloy melt (Fig. 14) combined with the boron-silicon oxide coating results in complete infiltration of the alloy melt into the fiber bundle (Fig. 15). Ultrasonic vibration is expected to enhance wetting of fibers in many situations and should be a valuable technique. We are currently investigating the mechanism of the enhancement as well as the mechanics of supplying the ultrasonic energy to the melt.
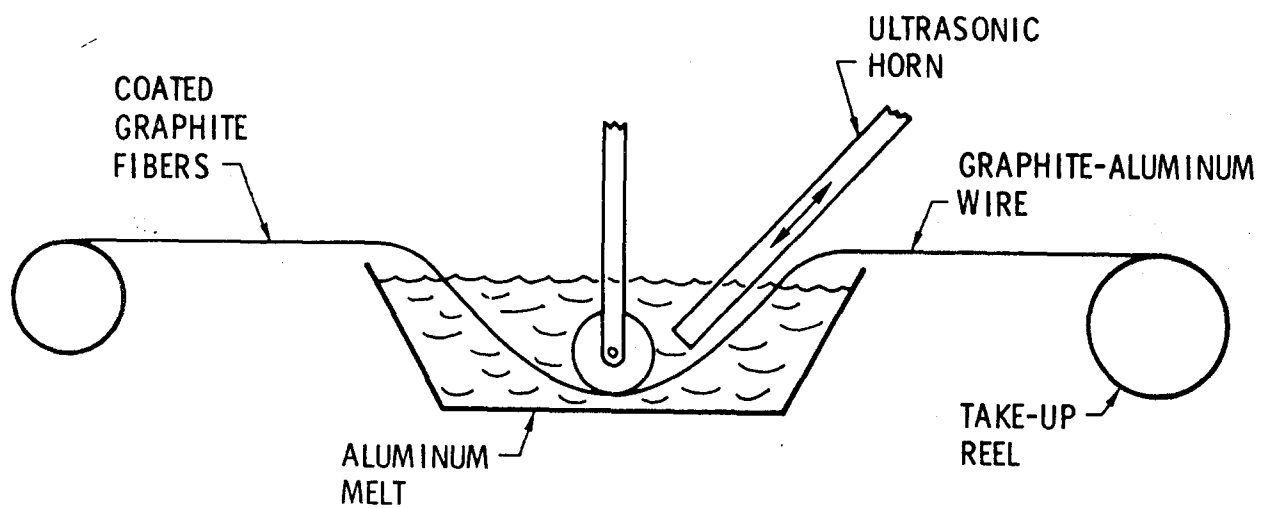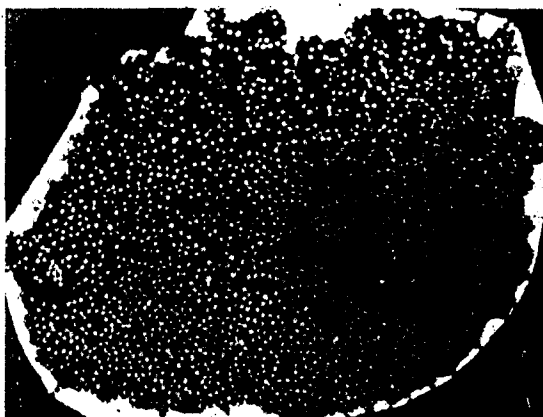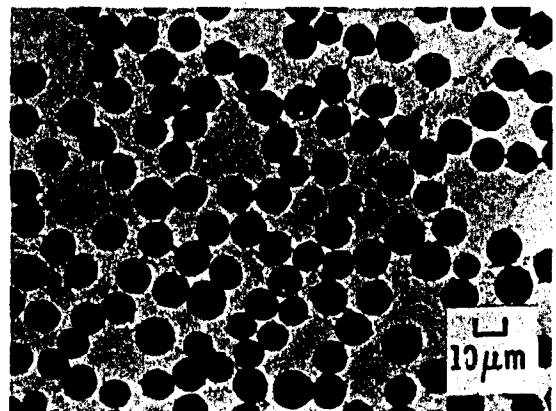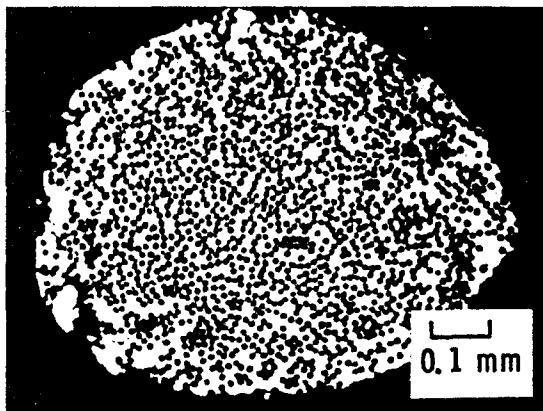
Fig. 14. Ultrasonic Vibration of Aluminum Melt to Assist Wetting of Coated Graphite Fibers

WITHOUT ULTRASONIC VIBRATION

WITH ULTRASONIC VIBRATION

Fig. 15.   Enhancement of Wetting by Ultrasonic Vibration.   P55 Fibers
Coated with Boron-Silicon Oxide in Aluminum-10% Magnesium Melt.

III. SUMMARY AND FUTURE NEEDS

It appears that it will soon be possible to deposit coatings on the fibers that will permit precise control of the mechanical properties of the interfacial material. The effect of this material on the mechanical properties of the composites must be better understood. For example, does a high modulus material at the interface provide better transverse or shear strength or better fracture toughness properties than a lower modulus material? Will materials with high damping capacity at the interface result in composites with better damping properties? How would these materials affect the coefficient of thermal expansion of the resultant composites? What kind of interface is best to prevent or retard corrosion of the composite?

Another concern is the strength of the interfacial bond between the fiber and the matrix. It is known that the bond must be strong enough to transfer the load to the fibers but that stronger bonds can lead to brittleness in ceramic matrix composites. What is the optimal bond strength in metal-matrix composites? How does the bonding affect the properties just mentioned? Also, what is the detailed chemistry of the bonding of the interfacial layer to both the fiber and the matrix?

For higher temperature applications, suitable diffusion barriers must be found to prevent the degradation of the fibers by reaction with the matrix. Coatings derived from organometallic precursors are good candidates for this application. The fabrication of inorganic materials from organometallic precursors is a new field and can be expected to yield many new potentially useful materials in the future.

To summarize, air-stable coatings for the fabrication of metal-matrix composites have been developed. A large variety of coatings from organometallic precursors have proved to be relatively easy to deposit. It is expected that these coatings will also be used in ceramic matrix composites.

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